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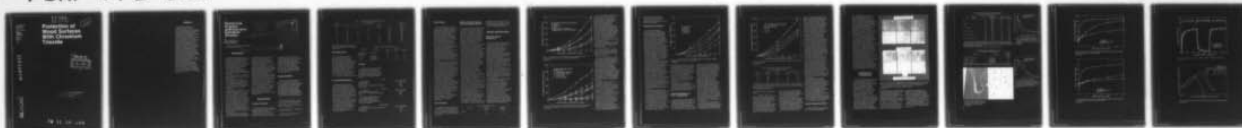
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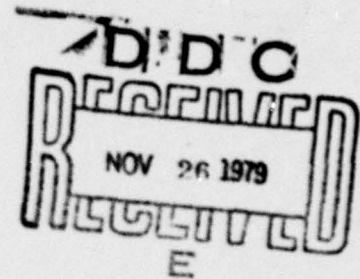
LEVEL II

Protection of Wood Surfaces With Chromium Trioxide

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Abstract

Wood surfaces treated with hexavalent chromium (Cr^{+6}) compounds have enhanced resistance to natural weathering properties. The performance of paints and stains applied to these treated wood surfaces is greatly improved. Degree of protection provided is directly related to Cr^{+6} concentration for chromium trioxide solutions (CrO_3 , chromic acid). A 4.8 percent CrO_3 solution is most effective at its original pH of 0.5. Surface treatment with CrO_3 reduces dimensional changes in wood exposed to water. Free water uptake of CrO_3 -treated wood is decreased to that observed after treatment with a water repellent. This decrease in free water uptake is found for treated flat-grained and vertical-grained surfaces but not for end-grain wood, indicating that capillary uptake still can occur. Water repellency was observed in both water-immersion and water-spray experiments. Preliminary studies on CrO_3 -treated wood surfaces using electron spectroscopy for chemical analysis show that Cr^{+6} is reduced to Cr^{+3} at concentrations of 1.25 percent chromium. The reduction undoubtedly plays a role in the fixation of Cr^{+6} on the wood surface.

PROTECTION OF WOOD SURFACES WITH CHROMIUM TRIOXIDE

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Forest Service research paper

Introduction

Many beneficial properties can be imparted to wood surfaces by treatment with aqueous solutions of certain inorganic chemicals (2,8).² Chemicals containing hexavalent chromium (Cr^{++}) are especially effective (1,2,6,11,15). Among the beneficial properties observed are the following:

- (1) Enhanced resistance to the natural outdoor weathering process (ultraviolet degradation and subsequent erosion) (2).
- (2) Control of staining or bleeding of water-soluble wood extractives through latex paints (6).
- (3) Improvement in durability of finishes on treated wood (3,11,12,15).
- (4) Reduction of swelling by water and increased water repellency (2).
- (5) Impartation of fungal resistance to the wood surface and to surface coatings (2).

While many Cr^{++} -containing compounds are beneficial in improving the surface properties of wood, only chromium trioxide (CrO_3 —also called chromic anhydride, or chromic acid when in aqueous solution) has been shown to be fixed on the wood surface after heat treatment (9). This fixation or "tying up" is especially important since Cr^{++} compounds are toxic. CrO_3 first interacts with wood components and then is both fixed and chemically reduced to the less hazardous trivalent state (Cr^{+3}); this process makes CrO_3 attractive as a potential pretreatment for wood surfaces.

The efficacy of CrO_3 treatment for improving several surface properties of wood has been demonstrated (2,3,6).

but detailed studies have not been performed. In addition, little is understood about the mechanisms responsible for the improvements observed in the performance of CrO_3 -treated wood surfaces.

This study investigated the natural weathering resistance of wood surfaces treated with aqueous solutions of CrO_3 as well as the performance of finishes applied to these treated surfaces.

Several treating variables (concentrations, pH, treatment method, temperature) were investigated as well as several wood species. The role of moisture repellency and dimensional stabilization in improving surface performance after CrO_3 treatment were investigated along with some preliminary assessments of the fate of Cr^{++} on the wood surface using the Electron Spectroscopy for Chemical Analysis (ESCA) technique (also described as Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy).

Experimental

Treating Chemicals

All treating solutions were prepared using distilled water and either U.S.P. or Reagent Grade chemicals. Concentrations were chosen which represented 0.625, 1.25, 2.5, and 5.0 percent chromium in solution as Cr^{++} .

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(For example, 4.8 pct CrO_3 would contain 2.5 pct chromium.) Composition of mixed copper and chromium treatments (hereafter called copper chromates for convenience) are shown in table 1. The ratio of copper to chromium in these compounds corresponds to ratios shown highly effective as wood surface treatments (2). Thus, they are of interest here for comparative purposes.

Treatment Method

Chemical solutions were applied to wood surfaces by immersion or by brush. Chemical pickup was determined by weighing before and after treatment. Brush application was at a rate of 0.1 milliliter of solution per 6.45 square centimeter of wood surface. Small specimens for accelerated exposure were treated by accurately pipetting the required amount of chemical solution onto the wood surface at the same rate

¹The author gratefully acknowledges the advice, suggestions, and laboratory assistance of Edward A. Mraz and Peter G. Sotos, and to Prof. Max Lagally at the University of Wisconsin-Madison, for performing ESCA experiments.

²Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

³Underlined numbers in parentheses refer to literature cited at end of report.

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Table 1.—Composition of treating solutions containing copper and chromium (molar ratio of Cu:Cr = 1)

Chemical treatment No.	Component, grams					Concentration of chromium
	CuSO ₄ · 5H ₂ O	Na ₂ Cr ₂ O ₇ · 2H ₂ O	CrO ₃	NH ₄ OH (30 pct NH ₃)	H ₂ O	
1-1	3.0	—	1.2	—	95.8	Pct
-2	6.0	—	2.4	—	91.6	0.625
-3	12.0	—	4.8	—	83.2	1.25
2-1	3.0	1.8	—	—	95.2	2.5
-2	6.0	3.6	—	—	90.4	.625
-3	12.0	7.2	—	—	80.8	1.25
3-1	3.0	—	1.2	5.9	89.9	2.5
-2	6.0	—	2.4	11.8	79.8	.625
-3	12.0	—	4.8	23.6	59.6	1.25
4-1	3.0	1.8	—	5.9	89.3	2.5
-2	6.0	3.6	—	11.8	78.6	.625
-3	12.0	7.2	—	23.6	57.2	1.25

used for brush application; the solution was then spread evenly over the surface with a glass rod.

Wood Specimens

Vertical-grained heartwood specimens of the following wood species were used in this study: Western redcedar (*Thuja plicata* Donn) and redwood (*Sequoia sempervirens* D. Don) Endl. Flat-grained and cross-section specimens of ponderosa pine (*Pinus ponderosa* var. *Ponderosa*) sapwood were used for water pickup studies. Specimen sizes and orientations are shown in table 2. All specimens were conditioned at 65 percent relative humidity (RH) and 27° C for at least 1 week before treating.

Accelerated Weathering

All specimens for accelerated weathering were exposed to a 6500-watt Xenon arc light source (which closely approximates natural sunlight spectrum in the visible and ultraviolet regions) in an enclosed chamber at 45° to 50° C. Exposure to this radiation alternated with a spray of distilled water at ambient temperatures with the light off. One week of accelerated weathering consisted of seven 24-hour cycles. Each cycle consisted of 4 hours of distilled water spray followed by 20 hours of light. Exposure times are expressed either as total days or as hours of light. Erosion of weathered wood was measured using the technique and specimen selection described earlier (10).

Table 2.—Size and type of specimens used

Evaluation	Type of specimen	Dimension		
		Tangential	Radial	Longitudinal
Finish performance	Vertical-grained	In.	In.	In.
Surface erosion	do	0.25	3	5
Water pickup	do	.25	1	1
Immersion	Flat-grained	1.5	.25	10
Do	Cross section	10	1.5	.25
Spray	Vertical-grained	.25	3	5
Do	Flat-grained	3	.25	5

Finishes

The performance of finishes applied over treated wood surfaces was evaluated as a function of chromium concentration and source by using laboratory-prepared oil-base and latex-base stains. Compositions were as follows:

Oil stain

Component	Percent by weight
Boiled linseed oil	60.0
Mineral spirits	28.5
Brown iron oxide pigment (50 pct solids)	10.3
Paraffin wax	1.2

Latex stain

Component	Percent by weight
Acrylic latex resin (50 pct solids)	25.0
Brown iron oxide pigment (50 pct solids)	12.5
Water	62.5

The degree of water repellency of wood surfaces treated with Cr⁺⁶ compounds was compared to a standard water repellent (WR) of the following composition:

Water repellent

Component	Percent by weight
Polyurethane exterior varnish (50 pct solids)	20.0
Paraffin wax	1.0
Mineral spirits	79.0

Water Pickup

The moisture repellency of CrO_3 -treated wood surfaces was investigated using several techniques. Standard swellometer cross sections (14) of ponderosa pine were treated with 4.8 percent CrO_3 solution (30-sec immersion). Additional swellometer specimens were cut from flat-grained ponderosa pine (table 2), and edges were sealed with three coats of aluminum-pigmented varnish (16). Surfaces were then treated with 4.8 percent CrO_3 solution by brush or immersion. Water pickup by spray was investigated on flat-grained and vertical-grained specimens of ponderosa pine and western redcedar. Moisture pickup by exposure to increased RH was investigated on flat-grained and vertical-grained specimens of western redcedar. Comparisons for all studies were made to untreated wood and to wood treated by immersion in the WR.

Swellometer tests (6 replicates) were performed using standard techniques (14,17). Water spray tests (3 replicates) were conducted in an exposure chamber with continuous distilled water spray. Samples (table 2) were removed from the chamber at regular intervals, dried between folds of absorbent paper, weighed, and then returned to the chamber. Average moisture pickup was determined for CrO_3 -treated, WR-treated, and untreated wood.

Adsorption of water vapor was determined by exposing treated and untreated wood specimens (3 replicates of each), previously conditioned at 30 percent RH, to 90 percent RH. After equilibrium had been reached, samples were again exposed to 30 percent RH until equilibrium was reached; the exposure cycle to 90 percent RH was then repeated. The relative effectiveness of the treatments in retarding adsorption of water vapor at 90 percent RH as compared to untreated controls was then determined.

Heat Treatment

All specimens in this study were first air-dried after CrO_3 treatment and then heated in an oven for 10 minutes at 135°C since earlier studies (9) showed that fixation of Cr^{+6} occurs under these conditions.

Electron Spectroscopy for Chemical Analysis (ESCA)

The ESCA technique has been shown to be useful in the surface analysis of paper and wood fiber (5). It is a unique tool both for the study of electronic structure and molecular bonding and also for the surface analysis of solids. In ESCA, a solid specimen placed on a mount in a high vacuum is irradiated with X-ray photons. Some of these photons collide elastically with inner shell electrons of atoms in the specimen. (In our studies, the electrons of interest were the $2p_{3/2}$ electrons of Cr^{+6} and Cr^{+3} on the treated wood surface.) After photon impact, electrons leave the atoms with a kinetic energy equal to that of the photon minus the binding energy which held the electron to its parent atom. This binding energy is different for every electronic shell of every element in the periodic table and it is possible to determine which elements and their valence state are present in the specimen by measuring the energy of emitted electrons. The technique is very sensitive to surface constituents (5); the energy of electrons emitted from a given elemental shell may be altered depending on the type of chemical bond formed by the element. In favorable circumstances, the chemical shift may indicate the type of chemical bonds present on the surface.

Small specimens of western redcedar were treated with increasing concentrations of CrO_3 in water at a rate of 0.016 milliliter per square centimeter of wood surface for this preliminary ESCA study. The samples were air-dried and heated in an oven for 10 minutes at 135°C (9). Solution concentrations are shown in table 3 along with concentrations of chromium on the wood surface realized from the treatment. Standard ESCA techniques were employed and a sample treated with Cr^{+3} (surface concentration of Cr , 0.4 mg/cm^2) was included. It was anticipated that treatment of wood surfaces with Cr^{+6} would yield Cr^{+3} due to oxidation of wood components and

subsequent reduction of the Cr^{+6} . The ESCA technique, if successful, should be able to distinguish between Cr^{+3} and Cr^{+6} on the treated wood surface.

Results and Discussion

Protection Against Weathering

Aqueous solutions containing Cr^{+6} , when applied to wood surfaces, provide a degree of protection against ultraviolet (UV) degradation (1,2,7). Accelerated weathering data for western redcedar specimens (fig. 1) surface-treated with five Cr^{+6} -containing compounds show that CrO_3 , acid copper chromate, and ammoniacal copper chromate are highly effective in protecting wood against UV degradation. (Similar results were found for redwood.) Of these three effective treatments, CrO_3 is perhaps the safest because heat treatment of wood surfaces treated with this chemical fixes virtually all measureable Cr^{+6} . This is in contrast to ammoniacal copper chromate, for example, where 2 percent soluble Cr^{+6} can be removed with water after heat treatment (9). A number of other wood species were also protected against UV degradation (weathering) by surface treatment with dilute solutions of CrO_3 (fig. 2) (2).

Springwood erosion rates for western redcedar treated with different concentrations of CrO_3 are shown in figure 3. The degree of protection provided against UV degradation is seen to be directly related to Cr^{+6} concentration over the range investigated. Treatment with 9.6 percent CrO_3 (equivalent to 5 pct Cr^{+6}) gave total protection for 10 weeks of accelerated weathering. This is equivalent to 2 to 3 years of outdoor weathering (10). Figure 3 also shows that UV protection is provided only for a limited time. After this protection period, degradation occurs at the same rate as observed for the untreated control.

Table 3.—Surface treatments for ESCA

Chemical	Chromium concentration	Surface concentration, Cr
	Pct	Mg/cm ²
CrCl_3 (Cr^{+3})	2.5	0.4
CrO_3 (Cr^{+6})	1.25	.2
	2.5	.4
	5.0	.8

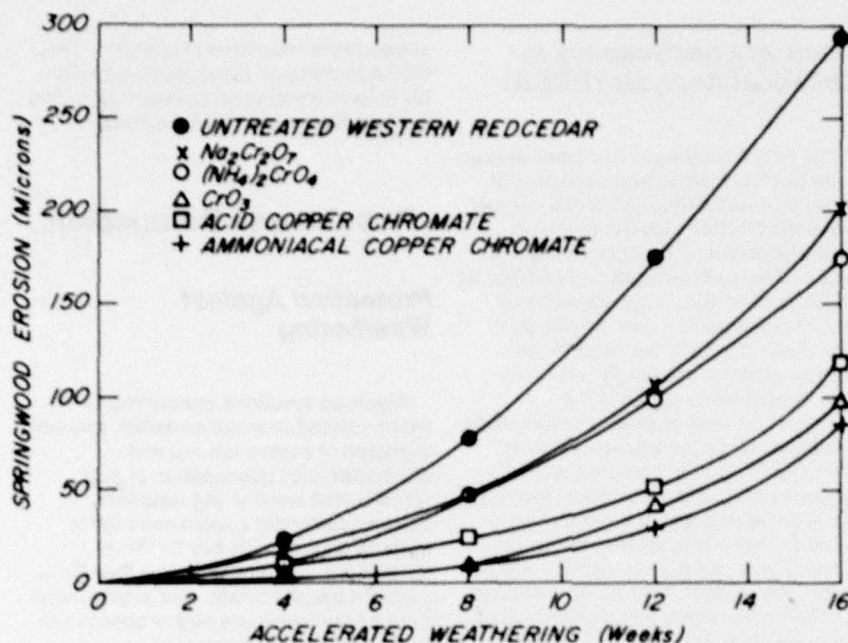


Figure 1.—Springwood erosion of western redcedar treated with five Cr* compounds (2.5 pct chromium)—accelerated weathering. (M 146 932)

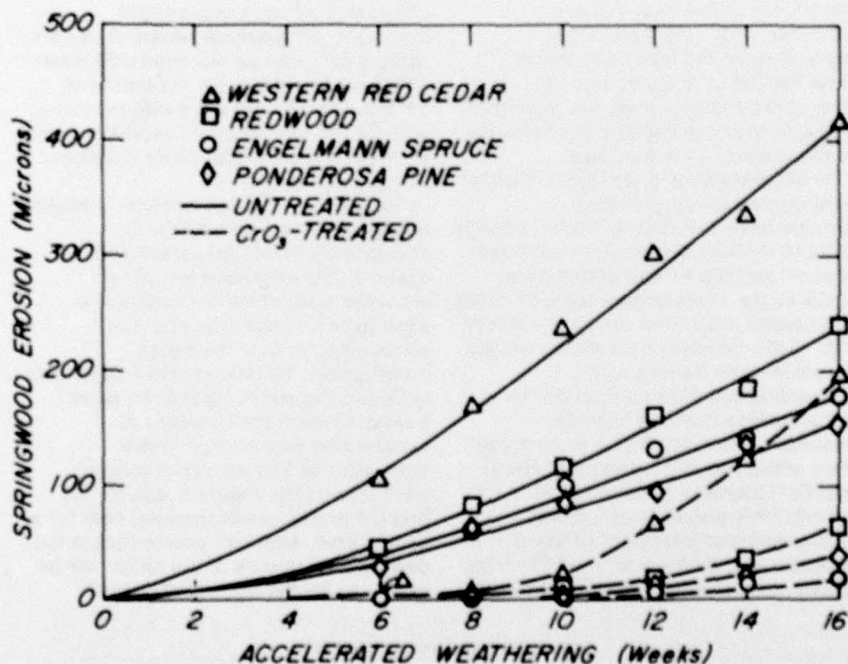
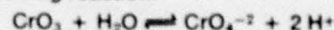


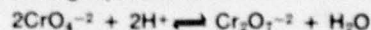
Figure 2.—Springwood erosion (accelerated weathering) of four wood species treated with 5.75 percent CrO₃ (3 pct Cr)—data of Black and Mraz (2). (M 146 931)

Solution pH affects the degree of UV protection (fig. 4). The pH of CrO₃ solutions was varied by addition of aqueous NH₄OH. The best protection was provided by the simple CrO₃ solution at its original pH of 0.5. Addition of NH₄OH resulted in decreased weathering effectiveness at pH of 2.6 as compared to a pH of 0.5. Improvement above the 2.6 value was found when NH₄OH was added to raise the solution pH to 8.8. Earlier results (2) had shown that ammoniacal copper chromate solutions were better than acid copper chromate solutions for UV protection. In the case of CrO₃, however, the most effective treatment is found when pH is 0.5.

The aqueous chemistry of Cr⁺⁶ is pH dependent. Initial dissolution of CrO₃ in water takes place according to the following reaction:



The chromate ion (CrO₄²⁻) exists at high pH. As pH is lowered, dichromate ions (Cr₂O₇²⁻) form according to the following equilibrium:



This equilibrium is quite labile. Acid solutions of dichromate are powerful oxidizing agents while chromate ion in basic solution is much less oxidizing. It appears as if oxidation of wood components by CrO₃ in water (pH = 0.5) is important in the protection mechanism. Since Cr⁺³ is the most stable oxidation state of chromium, this ion probably is formed when Cr⁺⁶ reacts with oxidizable wood components. The presence of Cr⁺³ (probably as oxides or as a complex) would explain the green color observed for Cr⁺⁶-treated wood surfaces after several days or weeks of exposure.

The reaction of Cr⁺⁶ with wood substance on the surface is undoubtedly complex. Rapid oxidation of easily oxidized wood constituents could occur on contact, during which Cr⁺⁶ would be rapidly reduced to Cr⁺³. Additional Cr⁺⁶ would then be adsorbed, along with additional acidic solvent. Various complexes of Cr⁺⁶ (or Cr⁺³ and intermediate mixed valence states) could form with wood components during this adsorption. The adsorption would minimize the mobility of the ions and thus reduce the reaction rates. However, the adsorbed ions are in a thermodynamically unstable state and the reactions must continue in order to reach the lowest energy state. Reaction rates will undoubtedly depend on

temperature, moisture content, anatomical factors, availability of reducing agents, and pH. UV irradiation could also play a role in the mechanism of fixation.

Performance of Finishes

The enhanced weathering performance of Cr^{+6} -treated wood surfaces subsequently finished with stains or paints has been described (2,3,11,15). Finish performance is directly related to Cr^{+6} concentration (table 4). Thus, a laboratory prepared oil-base stain (linseed oil) performed best over redwood or western redcedar when the wood surface had been treated with a solution containing 2.5 percent chromium. Similar results were observed with a laboratory-prepared latex stain. The finished wood samples are shown in figure 5 after 120 days of accelerated weathering (2,400 h xenon arc light). Generally, Cr^{+6} treatments work somewhat better on redwood than on western redcedar. At 2.5 percent Cr, however, performance is essentially equal for the two species.

Although addition of NH_3 (as NH_4OH) to copper chromate solution enhances performance (2), addition of NH_3 to CrO_3 solutions of varying concentration generally resulted in poorer stain performance after weathering, as compared to solutions without NH_3 (table 4). This was particularly true at the higher chromium concentration (2.5 pct) on both western redcedar and redwood. In addition, leaching of soluble chromium from the ammoniacal treatments occurred through the stain after a short time in the exposure chamber with the water spray portion of the exposure cycle. Earlier studies have shown that addition of NH_3 to CrO_3 solutions reduced fixation of Cr^{+6} and increased subsequent leaching by water (9).

The relative performance of CrO_3 versus $\text{Na}_2\text{Cr}_2\text{O}_7$ treatments as sources of Cr^{+6} on wood surfaces was also investigated. The individual compound performance was compared as well as combinations with CuSO_4 , with and without added NH_3 . The data (table 5) show that generally CrO_3 is more effective than $\text{Na}_2\text{Cr}_2\text{O}_7$ as the source of Cr^{+6} . Best performance with either chemical was found at a chromium concentration of 2.5 percent. Earlier observations (2) were confirmed in that ammoniacal copper chromate

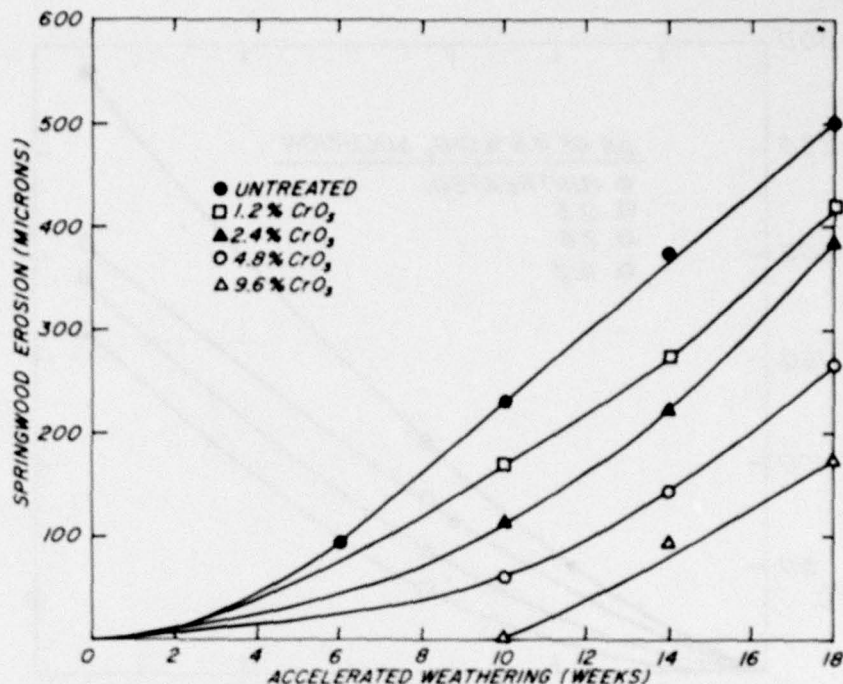


Figure 3.—Springwood erosion (accelerated weathering) of western redcedar treated with CrO_3 —effect of concentration. (M 146 934)

performed better than did acid copper chromate. Best finish performance was obtained with chromium concentration of 2.5 percent for CrO_3 and with ammoniacal copper chromates. These copper chromates (in reality mixtures of Cu^{+2} and Cr^{+6} compounds) are not totally fixed on the treated wood surface, and some leaching of heavy metals by H_2O was observed during the course of the accelerated exposure experiments.

Many of the CrO_3 treatments investigated by accelerated weathering techniques are being evaluated in outdoor exposure tests on several wood and wood-based substrates. Results will be reported in future publications.

Moisture Repellency of CrO_3 -Treated Wood

Black and Mraz (2) observed that the tangential swelling in cross sections of ponderosa pine sapwood in water was greatly reduced after 10 seconds' immersion in acid copper chromate or CrO_3 solutions (3 pct chromium). This was due, apparently, to a reduced water

absorption rate of the treated wood. Another factor contributing to the slow water uptake may be the increased contact angle of water with the treated wood surface; this is indicated by the spherical shape assumed by small drops of water on the surface of dry, CrO_3 -treated wood (fig. 6). Similar observations have been reported for copper-chrome-arsenic (CCA) preservative-treated wood (13). Chemical changes in the wood especially relative to polar hydroxyl functions are also most likely involved. Coetzee (4) found that the rate of moisture uptake from soil, resulting in moisture contents above the level critical for decay, was substantially reduced by treating wood samples with CCA preservative. Coetzee proposed that this retardation of moisture uptake was caused by a layer of insoluble CCA salts on the treated wood cell walls; this layer results in an increase in the structuring of water in contact with the wood surface.

The water-repellent effectiveness (WRE) of treated wood is determined by immersing the wood specimen in water and comparing the results to those for untreated wood (14). The WRE at any

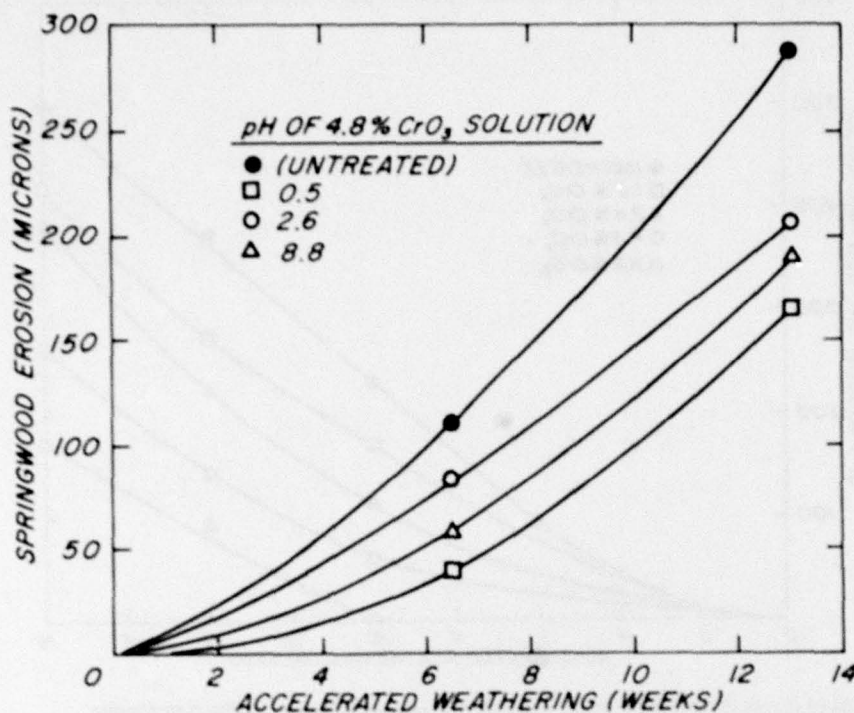


Figure 4.—Springwood erosion (accelerated weathering) of western redcedar with CrO_3 —effect of pH.
(M 146 935)

Table 4.—Performance of oil-base stain (accelerated weathering) over wood surfaces treated with CrO_3 —effect of concentration and addition of NH_3

CrO_3 concentration	Chromium concentration	pH of treating solution	Stain performance ¹	
			Redcedar	Redwood
Pct	Pct			
1.2	0.625	1.2	0	1.0
2.4	1.25	8	5	2.0
4.8	2.5	5	3.0	3.0
1.2	6.25	10.0	1.0	1.0
2.4	1.25	19.9	1.5	1.5
4.8	2.5	19.5	2.0	2.0

¹Performance values are difference between performance of untreated portion of sample and treated portion (fig. 5). A value of 5 indicates no weathering of treated portion. A value of 0 shows total loss of finish. Samples were exposed in an accelerated weathering chamber for 3,000 h xenon arc light with a schedule of 20 h light alternated with 4 h water spray.

²pH increased by addition of aqueous NH_3 .

given immersion time is calculated as follows:

$$\text{WRE} = \frac{S_c - S_T}{S_c} \times 100$$

where S_c equals the swelling observed for the control specimen and S_T the swelling for the treated specimen after immersion in water (all specimens preconditioned to 65 pct RH). Equilibrium values of WRE represent any dimensional stabilization resulting from the treatment. The WRE as a function of immersion time for cross sections of ponderosa pine sapwood which were CrO_3 treated is shown in

figure 7 along with the WRE obtained for the wax-containing, WR-treated wood. Both samples were immersed for 30 seconds in the treating solution. Chemical solution pickup was 75 percent for CrO_3 and 30 percent for the WR (table 6). Even with this increased chemical solution pickup, the WRE of CrO_3 -treated wood is considerably less than that for WR-treated wood (Fig. 7). The WR was more effective than CrO_3 even after 2 hours of water immersion.

When WRE was determined on flat-grained specimens with end-grain

sealed, the CrO_3 treatment was more effective initially than the WR treatment (fig. 8). This was expected, because water absorption on lateral wood surfaces would be less due to difficulty in wetting (fig. 6). The water repellency for CrO_3 -treated wood surfaces was observed even after 2 hours of water immersion (fig. 8) and compares favorably to that found for a standard WR after a similar time. This high WRE for CrO_3 - and WR-treated wood surfaces is found at relatively low chemical pickup compared to that found for cross sections at equal treating time (table 6). Dip treatment for 30 seconds resulted in about the same amount of chemical pickup as was found by brush application of CrO_3 at a rate of 0.1 milliliter solution per 6.45 square centimeters of wood surface.

The WRE was also evaluated using water spray. The results for ponderosa pine sapwood, flat-grained specimens (expressed as amount of water picked up by each specimen, fig. 9) show that in this case, a standard WR is considerably more effective than the CrO_3 treatment, particularly after 2 or more hours of spray time. Figure 10 shows that improved water repellency (lower water pickup) is found for western redcedar treated with CrO_3 as compared to ponderosa pine. With western redcedar, CrO_3 treatment is nearly equal to WR in water-repellent effectiveness, especially for water-spray periods up to 2 hours. The high extractives content of the wood, as well as differences in anatomical structure, may have an influence on the WRE of the treatment.

Although treatment of western redcedar with CrO_3 or WR is very effective at providing water repellency, the uptake of water vapor after CrO_3 treatment was relatively unchanged (fig. 11) as compared to untreated wood specimens. Similar results were observed using redwood. Ponderosa pine was not investigated but similar results would be expected. WR treatment is also ineffective in reducing water vapor uptake (16). Thus, it appears that water repellency observed for CrO_3 -treated wood is directly related to the increased contact angle of water with the treated wood surface (13).

Surface Analysis by ESCA

Preliminary ESCA experiments were performed on western redcedar

surfaces treated with CrO_3 solutions with concentrations of 2.4 to 9.6 percent (equivalent to 1.25 to 5 pct chromium). These treatments gave chromium surface concentrations of 0.2 to 0.8 milligram per square centimeter. The ESCA analyses were also made on a Cr^{+3} -treated wood surface for comparison (table 3). The expanded ESCA peaks for the $2p_{3/2}$ orbital electrons of Cr^{+3} and Cr^{+6} on the wood surface are shown in figure 12. These results show that at a concentration of 1.25 percent Cr (2.4 pct CrO_3 , 0.2 mg/cm^2 Cr) on the wood surface, all Cr^{+6} is converted by some reduction mechanism to Cr^{+3} and nearly identical curves result. At all chromium concentrations above 1.25 percent, ESCA curves are obtained, indicating a higher valence state of chromium, probably Cr^{+6} . These experiments show that it is quite possible to distinguish different valence states of chromium on wood surfaces. This technique should be useful in characterizing wood surfaces treated with various metal ions and can be used to determine the fate of these ions. Additional ESCA experiments are underway to determine the exact fate of Cr^{+6} on wood surfaces as a function of time, temperature, concentration, and wood species. These experiments also investigate the role that degree of penetration plays in improving durability of exposed wood surfaces, treated with Cr^{+6} compounds.

Summary and Conclusions

The results of this study indicate that CrO_3 is an effective source of Cr^{+6} for protection of wood surfaces. The degree of protection is directly related to Cr^{+6} concentration for both weathering protection against UV degradation and for improved performance of oil- and latex-based stains. The low pH of 0.5 for a 4.8 percent CrO_3 solution in water is apparently a necessity for best performance. Fixation of Cr^{+6} is also best at this pH, as shown in earlier work.

The CrO_3 -treated wood surfaces have improved UV resistance and a degree of water repellency and corresponding dimensional stability as compared to that of untreated wood. The CrO_3 treatment reduces the shrinkage, swelling, and free water absorption of the wood surface. This change may be

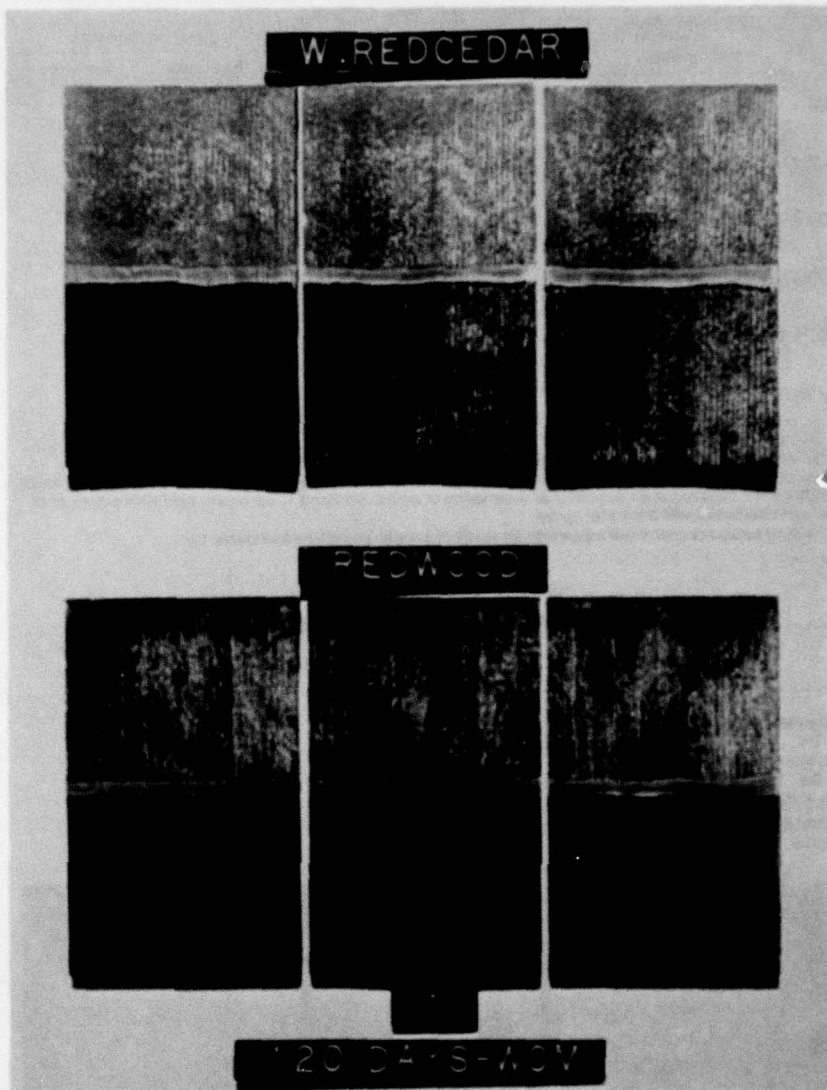


Figure 5.—Performance of oil-base stain on red cedar and redwood. Top portion of each wood panel was untreated and lower portion was treated with CrO_3 —left panel, 4.8 percent; center panel, 2.4 percent; right panel, 1.2 percent. Accelerated weathering—120 days (2,400 h of light). (M 145 278)

attributed to bulking as well as physico-chemical modifications of the cell wall in surface fibers by the penetrating chemical. These modifications could be a result of oxidation of wood components by CrO_3 to form carboxyl groups with accompanying reduction of Cr^{+6} to Cr^{+3} . Cross-linking or complex formation of Cr^{+3} with reactive functional groups such as the carboxyl would result in insolubilization and fixation of the chromium. The amount of CrO_3 on the wood surface directly

affects performance and water repellency. CrO_3 treatment has little effect on the pickup of water vapor. Preliminary ESCA experiments show that Cr^{+6} is reduced to Cr^{+3} on the wood surface at low CrO_3 concentrations. This suggests that the fixation of Cr^{+6} on the wood surface requires chemical oxidation-reduction reactions. Additional studies on the unique nature of Cr^{+6} wood surface treatments are continuing.

Table 5.—Performance of oil-base stain (accelerated weathering) over treated wood surfaces—comparison of CrO_3 and $\text{Na}_2\text{Cr}_2\text{O}_7$ as chromium source

Treatment group	pH	Chromium concentration Pct	Stain performance ^a	
			Redcedar	Redwood
CrO_3	1.2	0.625	0.5	1.0
	.8	1.25	1.0	2.0
	.5	2.5	2.5	3.0
$\text{Na}_2\text{Cr}_2\text{O}_7$	4.8	.625	0	.5
	4.7	1.25	.5	.5
	4.6	2.5	1.5	2.0
$\text{CrO}_3 + \text{CuSO}_4^b$	1.3	.625	0	2.0
	1.0	1.25	1.0	3.0
	.7	2.5	1.0	3.0
$\text{Na}_2\text{Cr}_2\text{O}_7 + \text{CuSO}_4^b$	4.1	.625	.5	1.0
	3.9	1.25	1.0	2.0
	3.6	2.5	2.5	3.0
$\text{CrO}_3 + \text{CuSO}_4 + \text{NH}_3^c$	8.8	.625	1.5	2.5
	8.8	1.25	1.5	2.5
	8.8	2.5	2.5	3.5
$\text{Na}_2\text{Cr}_2\text{O}_7 + \text{CuSO}_4 + \text{NH}_3^c$	9.5	.625	2.0	2.0
	9.5	1.25	2.0	2.0
	9.5	2.5	2.5	3.0

^aPerformance values are difference between performance of untreated portion of sample and treated portion (fig. 5). A value of 5 indicates no weathering of treated portion. A value of 0 shows total loss of finish. Samples were exposed in an accelerated weathering chamber for 3,000 h xenon arc light with schedule of 20 h light alternated with 4 h water spray.

^bTreating solutions contained equimolar amounts of copper and chromium (table 1).

Table 6.—Chemical pickup for treated ponderosa pine (30 sec immersion or brush applications)

Treatment	Sample type	Weight gain ^a after treatment
		Pct
Water repellent—immersion	Cross section	30
Do	Flat-grained	5
CrO_3 solution—immersion	Cross section	75
Do	Flat-grained	10
CrO_3 solution—brush	Flat-grained	6

^aPickup of treating solution based on original weight of sample conditioned at 65 pct RH. Average of 3 samples.

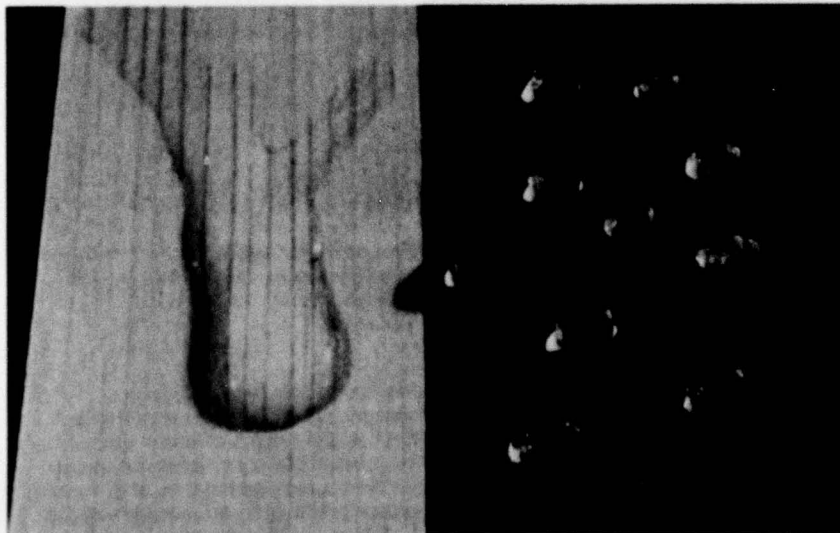


Figure 6.—Water repellency of CrO_3 treated surface (right) compared to untreated wood surface (left). (M 145 256)

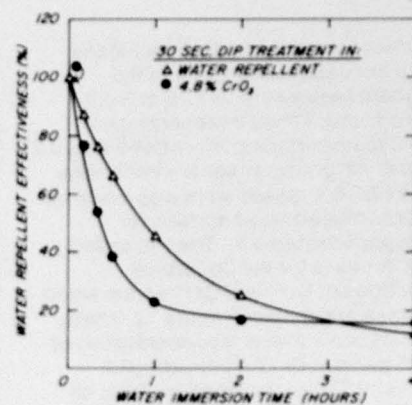


Figure 7.—Water repellent effectiveness of ponderosa pine cross sections treated with 4.8 percent CrO_3 or water repellent. (M 146 936)

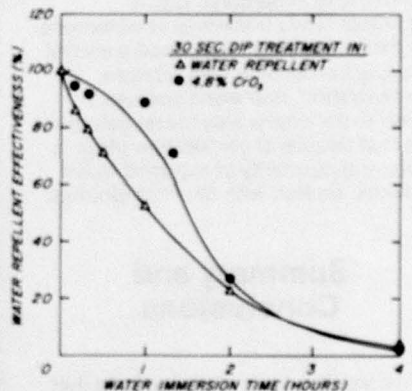


Figure 8.—Water repellent effectiveness of ponderosa pine treated with 4.8 percent CrO_3 or water repellent. Edge coated, flat-grained specimens. (M 146 930)

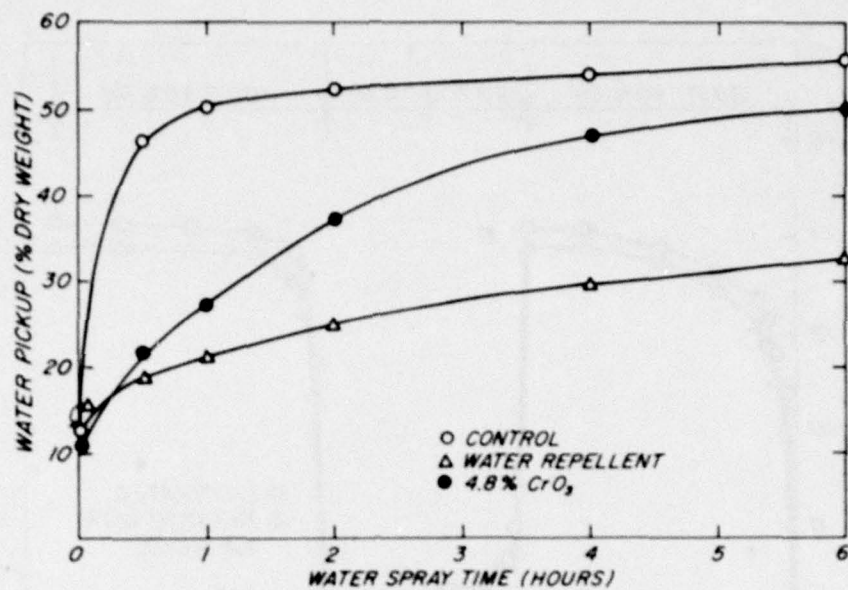


Figure 9.—Water pickup (spray) of ponderosa pine flat-grained sapwood treated with 4.8 percent CrO₃ or water repellent.
(M 146 938)

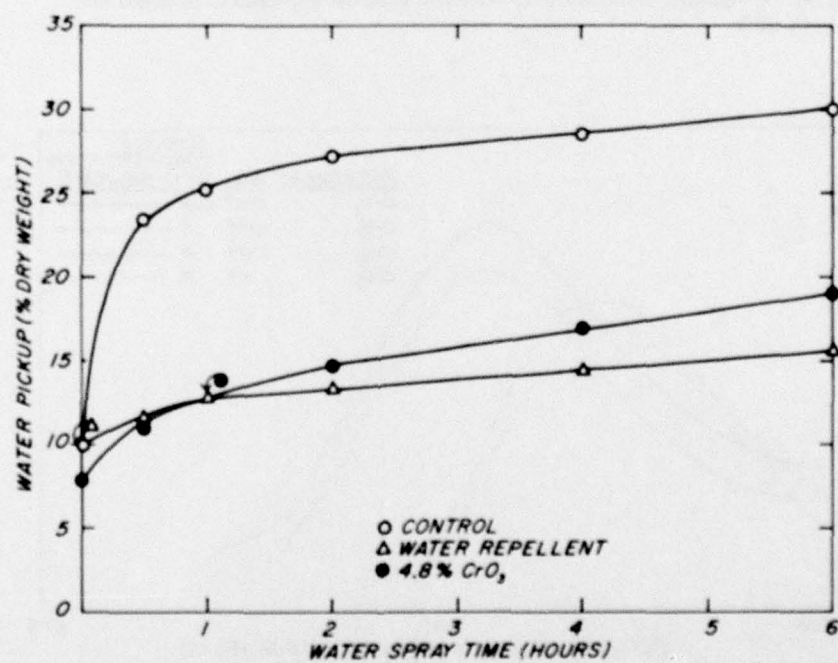


Figure 10.—Water pickup (spray) of western redcedar vertical-grained heartwood treated with 4.8 percent CrO₃ or water repellent.
(M 146 933)

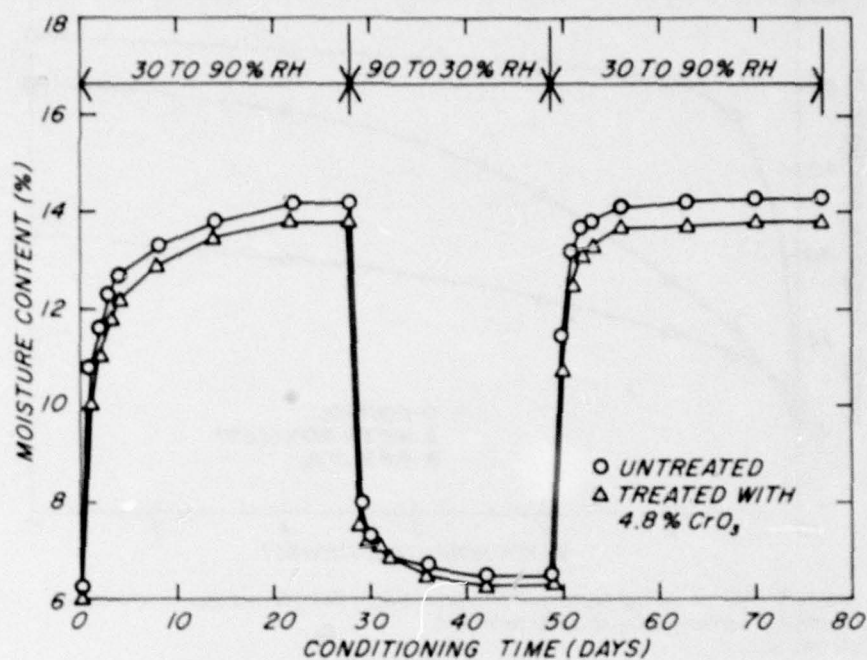


Figure 11.—Uptake of moisture for western redcedar exposed to different RH.
(M 146 937)

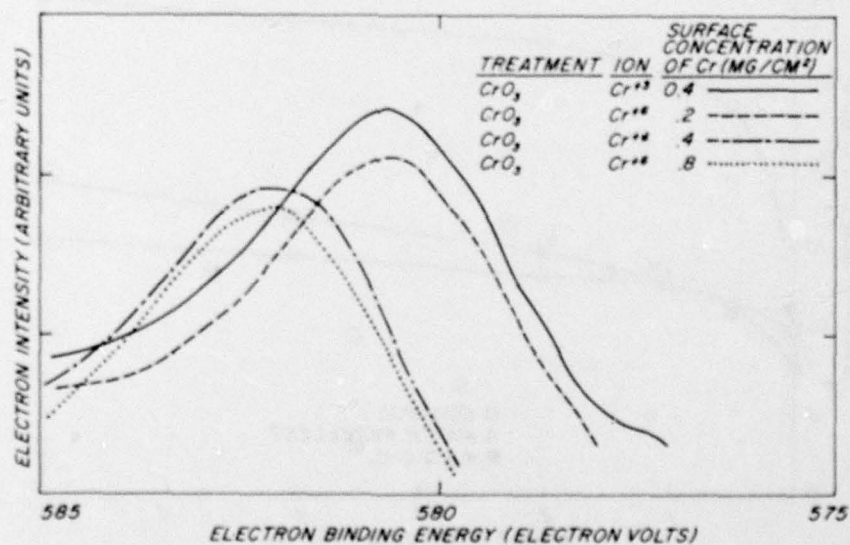


Figure 12.—Expanded ESCA peaks for Cr⁺³ (2p_{3/2}) on western redcedar surfaces.
(M 146 939)

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-- Cr(6+) --

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Protection of wood surfaces with chromium trioxide, by William C. Feist. Madison, Wis., 1979. Res. Pap. FPL 339, FPL, For. Serv., USDA, 12 p.

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